

THAT WHICH IS CLAIMED IS:

1. A method for carrying out the continuous polymerization of a monomer in a carbon dioxide reaction medium, said method comprising the steps of:

5 (a) providing an apparatus including a continuous reaction vessel and a separator;

(b) carrying out a polymerization reaction in said reaction vessel by combining a monomer, an initiator, and a carbon dioxide reaction medium therein, wherein said reaction medium comprises liquid or supercritical carbon dioxide, and wherein said reaction produces a solid polymer product in said reaction vessel; then

10 (c) withdrawing a continuous effluent stream from said reaction vessel during said polymerization reaction, wherein said continuous effluent stream is maintained as a liquid or supercritical fluid; then

(d) passing said continuous effluent stream through said separator and separating said solid polymer therefrom while maintaining said effluent stream as a
15 liquid or supercritical fluid; and then

(e) returning at least a portion of said continuous effluent stream to said reaction vessel while maintaining said effluent stream as a liquid or supercritical fluid at a pressure not more than about 100 psi less than the pressure in said reaction vessel, whereby the need for significant recompression of said continuous effluent stream
20 prior to return to said reaction vessel is minimized.

2. A method according to claim 1, wherein said polymerization reaction is selected from the group consisting of precipitation, microemulsion, emulsion, suspension, and dispersion polymerization reactions.
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3. A method according to claim 1, wherein said initiator is soluble in said liquid or supercritical reaction medium.

30 4. A method according to claim 3, wherein said initiator is toxic.

5. A method according to claim 1, wherein said reaction vessel is a stirred tank reactor.

6. A method according to claim 1, wherein said reaction vessel is an ideal stirred tank reactor.

7. A method according to claim 1, wherein said reaction vessel is a continuous loop reactor.

8. A method according to claim 1, wherein said reaction vessel is configured to provide a dimensionless exit age distribution ($E(\Theta)$) which reaches a maximum value between about $\Theta=0$ and about $\Theta=0.3$ and thereafter declines monotonically after reaching its maximum value.

9. A method according to claim 1, wherein said reaction vessel is configured to provide a cumulative exit age distribution (F) of from about 0.45 to about 0.70 when $\Theta=1$.

10. A method according to claim 1, wherein the monomer is a vinyl monomer.

11. A method according to claim 10, wherein the vinyl monomer is selected from the group consisting of an aromatic vinyl monomer, a conjugated diene monomer, an unsaturated acid monomer, a nitrogen-containing monomer, a non-aromatic unsaturated monocarboxylic ester monomer, and mixtures thereof.

12. A method according to claim 1, wherein the monomer is a fluorinated monomer.

13. A method according to claim 12, wherein the fluorinated monomer is selected from the group consisting of a fluoroacrylate monomer, a fluorostyrene monomer, a fluoroalkylene oxide monomer, a fluoroolefin monomer, and mixtures thereof.

14. A method according to claim 1, wherein the monomer is vinylidene fluoride.

15. A method according to claim 1, wherein the monomer is acrylic acid.

16. A method according to claim 1, wherein the polymer is a copolymer.

17. A method according to claim 1, wherein the initiator is a free radical initiator.

18. A method according to claim 17, wherein the initiator is selected from the group consisting of acetylcyclohexanesulfonyl peroxide; diacetyl peroxydicarbonate; diethyl peroxydicarbonate; dicyclohexyl peroxydicarbonate; di-2-ethylhexyl peroxydicarbonate; tert-butyl perneodecanoate; 2,2'-azobis(methoxy-2,4-dimethylvaleronitrile); tert-butyl perpivalate; dioctanoyl peroxide; dilauroyl peroxide; 2,2'-azobis(2,4-dimethylvaleronitrile); tert-butylazo-2-cyanobutane; dibenzoyl peroxide; tert-butyl per-2-ethylhexanoate; tert-butyl permaleate; 2,2'-azobis(isobutyronitrile); bis(tert-butylperoxy) cyclohexane; tert-butyl peroxyisopropylcarbonate; tert-butyl peracetate; 2,2-bis(tert-butylperoxy) butane; dicumyl peroxide; di-tert-amyl peroxide; di-tert-butyl peroxide; p-methane hydroperoxide; pinane hydroperoxide; cumene hydroperoxide; tert-butyl hydroperoxide; and mixtures thereof.

19. An apparatus for the continuous polymerization of a monomer in carbon dioxide; said apparatus comprising:

a continuous reaction vessel;

an effluent line connected to said reaction vessel;

a separator connected to said effluent line;

a return line connecting said separator to said reaction vessel so that liquid or supercritical reaction medium is returned to said reaction vessel from said separator while solid polymer is retained in said separator; and

control means for maintaining said reaction medium as a liquid or supercritical fluid in said separator and said return line and at a pressure not more than 100 psi different from the pressure in said reaction vessel during polymerization of monomer therein.

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20. An apparatus according to claim 19, wherein said separator is a filter.

21. An apparatus according to claim 19, wherein said separator comprises a plurality of filters in parallel with each other.

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22. An apparatus according to claim 19, wherein said separator comprises a rotating device therein .

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23. An apparatus according to claim 19, wherein said separator is a cyclone separator.

24. An apparatus according to claim 19, further comprising a filter positioned downstream of and in fluid communication with said cyclone separator.

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25. An apparatus according to claim 19, further comprising a cooler positioned on said effluent line between said reaction vessel and said control valve.

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26. An apparatus according to claim 19, further comprising a recirculation pump positioned on said return line between said first and second separators and said reaction vessel.

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27. An apparatus according to claim 19, further comprising a condenser positioned on said return line between said first and second separators and said reaction vessel.

28. An apparatus according to claim 19, wherein said reaction vessel is a stirred tank reactor.

29. An apparatus according to claim 19, wherein said reaction vessel is an ideal stirred tank reactor.

30. An apparatus according to claim 19, wherein said reaction vessel is a continuous loop reactor.

31. An apparatus according to claim 19, wherein said reaction vessel is configured to provide a dimensionless exit age distribution function ($E(\Theta)$) which reaches a maximum value between about $\Theta=0$ and about $\Theta=0.3$ and thereafter declines monotonically after reaching its maximum value.

32. An apparatus according to claim 19, wherein said reaction vessel is configured to provide a cumulative exit age distribution (F) of from about 0.45 to about 0.70 when $\Theta=1$.

33. A method for carrying out the continuous polymerization of a monomer in a carbon dioxide reaction medium, said method comprising the steps of:

(a) providing an apparatus including a continuous reaction vessel, a first separator, and a second separator;

(b) carrying out a polymerization reaction in said reaction vessel by combining a monomer, an initiator, and a carbon dioxide reaction medium therein, wherein said reaction medium comprises liquid or supercritical carbon dioxide, and wherein said reaction produces a solid polymer product in said reaction vessel; then

(c) withdrawing a continuous effluent stream from said reaction vessel during said polymerization reaction, passing said effluent stream through said first separator while maintaining said effluent stream as a liquid or supercritical fluid and separating said solid polymer therefrom; and then returning said effluent stream to said reaction vessel; and then

(d) withdrawing a continuous effluent stream from said reaction vessel during said polymerization reaction, passing said effluent stream through said second separator while maintaining said effluent stream as a liquid or supercritical fluid and separating said solid polymer therefrom, and then returning at least a portion of said

effluent stream to said reaction vessel, while concurrently removing said solid polymer separated in said first separator during said withdrawing step (c).

34. A method according to claim 33, wherein step (d) is followed by the
5 step of:

(e) repeating said withdrawing step (c) while concurrently removing said solid polymer separated in said second separator during said withdrawing step (d).

35. A method according to claim 33, wherein said polymerization reaction
10 is selected from the group consisting of precipitation, microemulsion, emulsion, suspension, and dispersion polymerization reactions.

36. A method according to claim 33, wherein said initiator is soluble in
15 said liquid or supercritical reaction medium.

37. A method according to claim 33, wherein said initiator is returned to
said reaction vessel in said reaction medium after said step of passing said effluent
stream through said separator.

38. A method according to claim 33, wherein said initiator is toxic.
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39. A method according to claim 33, wherein said reaction vessel is a
stirred tank reactor.

40. A method according to claim 33, wherein said reaction vessel is an
25 ideal stirred tank reactor.

41. A method according to claim 33, wherein said reaction vessel is a
30 continuous loop reactor.

42. A method according to claim 33, wherein said reaction vessel is configured to provide a dimensionless exit age distribution function ($E(\Theta)$) which reaches a maximum value between about $\Theta=0$ and about $\Theta=0.3$ and thereafter declines monotonically after reaching its maximum value.

43. A method according to claim 33, wherein said reaction vessel is configured to provide a cumulative exit age distribution (F) of from about 0.45 to about 0.70 when $\Theta=1$.

44. A method according to claim 33, wherein the monomer is a vinyl monomer.

45. A method according to claim 44, wherein the vinyl monomer is selected from the group consisting of an aromatic vinyl monomer, a conjugated diene monomer, an unsaturated acid monomer, a nitrogen-containing monomer, a non-aromatic unsaturated monocarboxylic ester monomer, and mixtures thereof.

46. A method according to claim 33, wherein the monomer is a fluorinated monomer.

47. A method according to claim 46, wherein the fluorinated monomer is selected from the group consisting of a fluoroacrylate monomer, a fluorostyrene monomer, a fluoroalkylene oxide monomer, a fluoroolefin monomer, and mixtures thereof.

48. A method according to claim 33, wherein the monomer is vinylidene fluoride.

49. A method according to claim 33, wherein the monomer is acrylic acid.

50. A method according to claim 33, wherein the polymer is a copolymer.

51. A method according to claim 33, wherein the initiator is a free radical initiator.

52. A method according to claim 51, wherein the initiator is selected from the group consisting of acetylcyclohexanesulfonyl peroxide; diacetyl peroxydicarbonate; diethyl peroxydicarbonate; dicyclohexyl peroxydicarbonate; di-2-ethylhexyl peroxydicarbonate; tert-butyl perneodecanoate; 2,2'-azobis(methoxy-2,4-dimethylvaleronitrile); tert-butyl perpivalate; dioctanoyl peroxide; dilauroyl peroxide; 2,2'-azobis(2,4-dimethylvaleronitrile); tert-butylazo-2-cyanobutane; dibenzoyl peroxide; tert-butyl per-2-ethylhexanoate; tert-butyl permaleate; 2,2-azobis(isobutyronitrile); bis(tert-butylperoxy) cyclohexane; tert-butyl peroxyisopropylcarbonate; tert-butyl peracetate; 2,2-bis(tert-butylperoxy) butane; dicumyl peroxide; di-tert-amyl peroxide; di-tert-butyl peroxide; p-methane hydroperoxide; pinane hydroperoxide; cumene hydroperoxide; tert-butyl hydroperoxide; and mixtures thereof.

53. An apparatus for the continuous polymerization of a monomer in carbon dioxide; said apparatus comprising:

- a continuous reaction vessel;
- an inlet line connected to the reaction vessel;
- an effluent line connected to said reaction vessel;
- an inlet control valve connected to said effluent line;
- a first separator and a second separator connected to said inlet control valve, said control valve switchable between (i) a first position in which said first separator is in fluid communication with said effluent line while said second separator is not, and (ii) a second position in which said second separator is in fluid communication with said effluent line while said first separator is not; and
- a return line connecting each of said first and second separators to said reaction vessel so that liquid or supercritical reaction medium is returned to said reaction vessel from said separators while solid polymer is retained in said separator; and

control means operatively associated with said return line for maintaining said reaction medium as a liquid or supercritical fluid in said first and second separators;

whereby effluent from said continuous reaction vessel can be (i) continuously passed through said first separator while polymer may be removed from said second separator by switching said inlet control valve to said first position, and (ii) continuously passed through said second separator while polymer may be removed from said first separator by switching said inlet control valve to said second position

54. An apparatus according to claim 53, wherein said first and second separators are filters.

55. An apparatus according to claim 53, wherein said first and second separators are cyclone separators.

56. An apparatus according to claim 53, further comprising filters respectively positioned downstream of and in fluid communication with each of said cyclone separator.

57. An apparatus according to claim 53, wherein said separator comprises a plurality of filters in parallel with each other.

58. An apparatus according to claim 53, wherein said separator comprises a rotating device therein.

59. An apparatus according to claim 53, further comprising a cooler positioned on said effluent line between said reaction vessel and said control valve.

60. An apparatus according to claim 53, further comprising a recirculation pump positioned on said return line between said first and second separators and said reaction vessel.

61. An apparatus according to claim 53, further comprising a condenser positioned on said return line between said first and second separators and said reaction vessel.

5 62. An apparatus according to claim 53, further comprising:
an outlet control valve connected to said return line; and
an outlet line connecting each of said separators to said outlet control valve;
said outlet control valve switchable between (i) a first position in which said
first separator is in fluid communication with said return line while said second
10 separator is not, and (ii) a second position in which said second separator is in fluid
communication with said return line while said first separator is not.

63. An apparatus according to claim 62, further comprising:
control means for concurrently switching said inlet and outlet control valves to
15 said first positions; and concurrently switching said inlet and outlet control valves to
said second positions.

64. An apparatus according to claim 53, wherein said reaction vessel is a
stirred tank reactor.
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65. An apparatus according to claim 53, wherein said reaction vessel is an
ideal stirred tank reactor.

66. An apparatus according to claim 53, wherein said reaction vessel is a
25 continuous loop reactor.

67. An apparatus according to claim 53, wherein said reaction vessel has a
dimensionless exit age distribution function ($E(\Theta)$) which reaches a maximum value
between about $\Theta=0$ and about $\Theta=0.3$ and thereafter declines monotonically after
30 reaching its maximum value.

68. An apparatus according to claim 53, wherein said reaction vessel is configured to provide a cumulative exit age distribution (F) of from about 0.45 to about 0.70 when $\Theta=1$.

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